

X-Ray Diffraction Study of the $\text{GdM}^{\text{II}}\text{CoO}_{3.5}$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) Cobaltites

E. S. Mustafin, D. A. Kaikenov, A. M. Pudov, Kh. B. Omarov,
D. Zh. Karabekova, and B. Sh. Sarsenbaev

Buketov State University, Universitetskaya ul. 28, Karaganda, 100028 Kazakhstan

e-mail: edigemus@mail.ru

Received January 28, 2015; in final form, April 24, 2015

Abstract—Four compounds with the general formula $\text{GdM}^{\text{II}}\text{CoO}_{3.5}$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) have been prepared for the first time by high-temperature solid-state reactions between gadolinium(III) oxide, cobalt(II) oxide, and alkaline-earth carbonates. Their crystal class and unit-cell parameters have been determined by X-ray diffraction.

DOI: 10.1134/S0020168515120080

INTRODUCTION

Recent years have seen a number of emerging industrial applications for electrochemical devices operating at elevated ($t > 300^\circ\text{C}$) and high ($t > 1000^\circ\text{C}$) temperatures: solid electrolyte fuel cells, oxygen sensors, electrolyzers for oxygen generation, oxygen pumps, and others. However, no suitable materials for oxygen electrodes or switches, capable of replacing metals in such devices, have yet been proposed. Such materials should be stable in chemically aggressive media at high temperatures and possess sufficient electrical conductivity. Perovskite-like oxides with the general formula $\text{ABO}_{3\pm\delta}$ ($\text{A} = \text{Ca}, \text{Pb}, \text{La}$ and other metals; $\text{B} = \text{Al}, \text{Mn}, \text{Fe}, \text{Co}$, and other metals) are promising materials possessing unique properties, such as high-temperature ionic conductivity, colossal magnetoresistance, and catalytic activity [1–3].

In this paper, we report the synthesis and X-ray diffraction characterization of alkaline-earth rare-earth cobaltites with the general formula $\text{GdM}^{\text{II}}\text{CoO}_{3.5}$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$), which possess attractive physical (semiconducting, ferroelectric, magnetic, superconducting, and other) properties.

EXPERIMENTAL PROCEDURE AND RESULTS

The cobaltites were prepared by standard solid-state reactions in three steps at different temperatures. The starting chemicals used were gadolinium oxide (extrapure grade), cobalt(II) oxide (reagent grade), and alkaline-earth carbonates (reagent grade). Appropriate amounts of the starting materials were weighed out to the fourth decimal place. The starting-mixture compositions were adjusted to give the final compositions of the mixed ferrites. The mixtures were thoroughly ground in an agate mortar and then reacted in Alundum crucibles placed in a Silit furnace. The syn-

thesis process comprised firing at 800°C for 10 h, then at 1300°C for 10 h with several intermediate grindings in a mortar, and finally at 400°C for 20 h in order to obtain compounds stable under ordinary conditions.

X-ray diffraction measurements were performed on a DRON-2.0 powder diffractometer (CuK_α radiation, $V = 30 \text{ kV}$, $I = 10 \text{ mA}$, counter range of 1000 cps, continuous scan rate of $2^\circ/\text{min}$, time constant of 5 s, $2\theta = 10^\circ - 90^\circ$). The X-ray powder diffraction patterns of the new cobaltites were indexed by the homology method [4] in the perovskite structure type. The density of the cobaltites was determined by the Archimedes method [5] using 1-mL glass pycnometers. Tetrabromoethane was used as a saturating and suspending medium, because it adequately wets the cobaltites in question and is nonreactive with them, and its density varies little with temperature. The density of each compound was obtained as the average over three repeated measurements.

The synthesized compounds were analyzed for cobalt by atomic absorption (Table 1).

A comparative analysis of calculation results and experimental data showed that the compounds had the intended compositions.

The validity of the indexing schemes derived from our X-ray diffraction data was confirmed by satisfactory agreement between the observed and calculated $10^4/d^2$ values (Table 2).

According to the above indexing results, the cobaltites crystallize in tetragonal symmetry and have a distorted perovskite structure. The satisfactory agreement between the X-ray and measured densities of the cobaltites (Table 3) suggests that the proposed indexing schemes are correct and that the lattice parameters were determined with adequate accuracy.

The increase in ionic radius in going from magnesium to barium is accompanied by nonmonotonic

Table 1. Cobalt content of the synthesized compounds

Compound	Weight percent Co	
	nominal	atomic absorption data
GdMgCoO _{3.5}	19.87	19.2
GdCaCoO _{3.5}	18.88	18.52
GdSrCoO _{3.5}	16.37	16.1
GdBaCoO _{3.5}	14.38	13.98

Table 2. Indexing schemes for the X-ray powder diffraction patterns of GdM^{II}CoO_{3.5} (M^{II} = Mg, Ca, Sr, Ba)

<i>I</i> , %	<i>d</i> , Å	10 ⁴ / <i>d</i> _{obs} ²	<i>hkl</i>	10 ⁴ / <i>d</i> _{calc} ²
GdMgCoO _{3.5}				
23	2	513.2	113	502.63
13	3.752	710.4	221	724.27
100	3.115	1030.6	223	1018.27
53	2.928	1166.4	321	1153.97
27	2.889	1198.1	313	1190.15
16	2.792	1282.8	224	1275.52
24	2.749	1323.3	006	1323.00
65	2.702	1369.7	040	1375.04
11	2.544	1545.1	330	1546.92
10	2.395	1743.4	126	1752.70
11	2.295	1898.6	017	1886.69
12	2.223	2023.6	235	2035.97
17	2.118	2229.2	127	2230.45
16	2.072	2329.3	424	2306.80
7	2.006	2485.1	227	2488.27
10	1.938	2662.5	317	2660.15
45	1.908	2746.9	440	2750.08
8	1.745	3284.0	417	3261.73
15	1.694	3484.8	621	3474.35
9	1.665	3607.2	622	3584.60
33	1.627	3777.7	623	3768.35
10	1.592	3945.6	057	3949.25
10	1.576	4026.1	624	4025.60
13	1.557	4125.0	544	4111.54
5	1.528	4283.1	257	4293.01
8	1.467	4646.6	713	4627.75
5	1.441	4815.8	643	4799.63
5	1.375	5289.3	0012	5292.00
9	1.349	5495.1	080	5500.16
5	1.33	5653.2	082	5647.16
5	1.31	5827.2	564	5830.34
5	1.255	6349.1	277	6355.57
9	1.238	6524.7	663	6518.43
7	1.206	6875.5	840	6875.20

Table 2. (Contd.)

$I, \%$	$d, \text{\AA}$	$10^4/d_{\text{obs}}^2$	hkl	$10^4/d_{\text{calc}}^2$
$\text{GdCaCoO}_{3.5}$				
13	4.414	513.3	202	512.5
14	3.726	720.3	220	719.0
8	3.551	793.0	114	791.8
40	3.114	1031.2	312	1051.8
8	2.928	1166.4	320	1168.4
93	2.694	1377.9	006	1377.0
100	2.636	1439.2	400	1438.1
12	2.526	1567.2	116	1556.8
8	2.179	2106.1	226	2096.0
13	2.133	2198.0	306	2185.9
6	2.064	2347.4	510	2336.9
16	1.978	2555.9	326	2545.4
21	1.955	2616.4	118	2627.8
18	1.906	2752.7	425	2753.9
5	1.863	2881.2	440	2876.2
10	1.817	3028.9	327	3042.7
3	1.75	3265.3	308	3256.9
11	1.655	3650.9	534	3667.9
13	1.626	3782.3	0.0.10	3825.0
9	1.572	4046.6	630	4044.6
16	1.541	4211.1	517	4211.1
22	1.526	4294.3	615	4281.8
22	1.511	4380.0	633	4388.9
9	1.35	5487.0	650	5482.7
9	1.319	5747.9	800	5752.3
4	1.306	5862.9	2.0.12	5867.5
5	1.281	6094.0	803	6096.6
5	1.236	6545.8	830	6561.2
12	1.182	7157.6	6.1.10	7150.6
$\text{GdSrCoO}_{3.5}$				
15	3.726	720.3	220	716.3
10	3.587	777.2	114	788.4
12	3.349	891.6	130	895.4
29	3.115	1030.6	015	1041.5
42	2.749	1323.3	224	1325.6
74	2.701	1370.7	006	1370.9
100	2.642	1432.6	400	1432.6
14	2.464	1647.1	331	1649.8
10	2.3	1890.4	007	1865.9
13	2.235	2001.9	044	2041.9
24	2.133	2198.0	036	2176.7
18	2.078	2315.8	217	2313.6
17	1.999	2502.5	512	2480.4

Table 2. (Contd.)

$I, \%$	$d, \text{\AA}$	$10^4/d_{\text{obs}}^2$	hkl	$10^4/d_{\text{calc}}^2$
27	1.906	2752.7	522	2749.0
42	1.875	2844.4	054	2847.8
20	1.8	3086.4	009	3084.5
17	1.656	3646.5	354	3653.6
17	1.628	3773.0	229	3800.8
12	1.596	3925.9	623	3924.3
34	1.55	4162.3	0.2.10	4166.2
30	1.537	4233.0	428	4227.9
7	1.379	5258.6	464	5265.4
12	1.378	5266.3	644	5265.4
17	1.336	5602.6	4.2.10	5598.8
10	1.233	6577.7	831	6574.5
14	1.204	6898.4	178	6914.1
$\text{GdBaCoO}_{3.5}$				
23	4.414	513.2	113	502.6
13	3.752	710.4	221	724.3
100	3.115	1030.6	223	1018.3
53	2.928	1166.4	321	1154.0
27	2.889	1198.1	313	1190.2
16	2.792	1282.8	224	1275.5
24	2.749	1323.3	006	1323.0
65	2.702	1369.7	040	1375.0
11	2.544	1545.1	330	1546.9
10	2.395	1743.4	126	1752.7
11	2.295	1898.6	017	1886.7
12	2.223	2023.6	235	2036.0
17	2.118	2229.2	127	2230.5
16	2.072	2329.3	424	2306.8
7	2.006	2485.1	227	2488.3
10	1.938	2662.5	317	2660.2
45	1.908	2746.9	440	2750.1
8	1.745	3284.0	417	3261.7
15	1.694	3484.8	621	3474.4
9	1.665	3607.2	622	3584.6
33	1.627	3777.7	623	3768.4
10	1.592	3945.6	057	3949.3
10	1.576	4026.1	624	4025.6
13	1.557	4125.0	544	4111.5
5	1.528	4283.1	257	4293.0
8	1.467	4646.6	713	4627.8
5	1.441	4815.8	643	4799.6
5	1.375	5289.3	0.0.12	5292.0
9	1.349	5495.1	080	5500.2
5	1.330	5653.2	082	5647.2
5	1.310	5827.2	564	5830.3
5	1.255	6349.1	277	6355.6
9	1.238	6524.7	663	6518.4
7	1.206	6875.5	840	6875.2

Table 3. Lattice parameters and density of the synthesized cobaltites (tetragonal symmetry, $Z = 16$)

Compound	Lattice parameters, Å		$V, \text{Å}^3$	$V_{\text{subcell}}, \text{Å}^3$	Density, g/cm ³	
	a	c			X-ray	measured
GdMgCoO _{3.5}	10.54	16.25	1805.79	225.72	4.361	4.358
GdCaCoO _{3.5}	10.55	16.17	1798.96	224.87	4.610	4.595
GdSrCoO _{3.5}	10.56	16.20	1809.81	226.23	5.280	5.276
GdBaCoO _{3.5}	10.79	16.49	1919.45	239.93	5.667	5.660

variations in the lattice parameters of the cobaltites (Table 3), which seems to be due to secondary periodicity in the Periodic Group.

Thus, the GdMgCoO_{3.5}, GdCaCoO_{3.5}, GdSrCoO_{3.5}, and GdBaCoO_{3.5} cobaltites have been prepared for the first time by solid-state reactions and their crystallographic parameters have been determined.

REFERENCES

1. Pal'guev, S.F., Gil'derman, V.K., and Zemnov, V.I., *Vysokotemperaturnye oksidnye elektronnye provodniki dlya elektrokhimicheskikh ustroystv* (High-Temperature Electronic Oxide Conductors for Electrochemical Applications), Moscow: Nauka, 1990.
2. Nadeev, A.N., Tsybulya, S.V., Gerasimov, E.Yu., et al., Structural features of the formation of $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\sigma}$ ($0 < x < 0.7$), *J. Struct. Chem.*, 2010, vol. 51, no. 5, pp. 891–897.
3. Nemudryi, A.P., Koroleva, O.N., Pavlyukhin, Yu.T., et al., Synthesis and physicochemical properties of strontium cobaltite-based perovskites, *Izv. Akad. Nauk, Ser. Fiz.*, 2003, vol. 67, no. 7, pp. 952–954.
4. Kovba, L.M. and Trunov, V.K., *Rentgenofazovyi analiz* (Phase Analysis by X-Ray Diffraction), Moscow: Mosk. Gos. Univ., 1976, 2nd ed.
5. Kivilis, S.S., *Tekhnika izmerenii plotnosti zhidkosti i tverdykh tel* (Techniques for Measuring Densities of Liquids and Solids), Moscow: Standartgiz, 1959.

Translated by O. Tsarev